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ADSORPTION OF OXYGEN ON THE TUNGSTEN (110) PLANE AT LOW TEMPERA--ETC(U)

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ABSTRACT

The adsorption of oxygen on the W(110) plane was carried out at 26 K and investigated by means of ultraviolet and X-ray photoelectron spectroscopy. It was found that atomic oxygen is adsorbed first to essentially saturation coverage ($\theta/W=0.6$) before adsorption of molecular oxygen occurs. The spectrum of the latter is very similar to that of gas phase O_2 but the shift to weaker binding energies is greater for the $1s$ level than for the valence orbitals.

It is generally believed that the dissociative adsorption of diatomic molecules proceeds via a weakly bound undissociated precursor. The principal evidence for the latter has come from the shape of sticking coefficient vs. coverage isotherms. Some attempts to look more directly for precursors at very low temperature have also been made.

Chottiner and Glover¹ adsorbed oxygen on thin Sn films at 5 K, and concluded from resistance measurements that oxygen was initially adsorbed in a physisorbed, molecular state which converted at 13 K to a chemisorbed atomic state. Gland² adsorbed oxygen on Pt(111) and Pt (S)-12(111)x(111) surfaces and found from isotope exchange and chemical titration experiments that little or no dissociation of adsorbed molecules oxygen occurred below 150K. Bradshaw, et al³, using UPS, found initially dissociative adsorption up to half monolayer coverage, followed by molecular physisorption at higher coverages for oxygen on Al (111). Leung and Gomer⁴ adsorbed oxygen on W(110) at 20 K and found that the layer so formed showed an increase in work function, together with desorption of part of the layer of heating to 45 K. They also

noted that electron stimulated desorption of the 20 K layer produced O^+ only after an induction period. They interpreted these results as the existence of a molecular precursor layer which converted on heating to 45 K to an atomic layer with desorption of the excess as O_2 . They also noted, however, that readsorption on an atomic layer at 20 K led to formation of a weakly bound molecular species, $\alpha-O_2$, which desorbed at 45 K. Wang and Gomer⁵ showed that the coverage of the atomic layer obtained by adsorption at 20 K and heating to 45 was $\theta/W = 0.62$ or 8.8×10^{14} O atoms/cm² and that the maximum amount of O_2 desorbing at 45 K was 4.4×10^{14} O_2 molecules/cm².

The purpose of the present work was to look for the precursor state by means of UPS and XPS. It was found, however, that at 25 K, the lowest temperature accessible to us, an atomic layer formed, with O_2 adsorption occurring only after completion of the atomic layer. In a separate publication⁶ we present evidence from isotopic labelling experiments that this is also the case at 20 K, so that the interpretation of Leung and Gomer is incorrect.

EXPERIMENTAL

The experiments were carried out in a stainless steel ultrahigh vacuum system, described in detail previously⁷, equipped with the following: a Varian 4-grid Leed system and Vacuum Generators capillary He resonance lamp for UPS measurements by means of retardation analysis; a Physical Electronics double pass cylindrical mirror analyzer for differential energy analysis of Auger and X-ray photoelectrons. For the latter a Physical Electronics X-ray source with Mg anode was used. The system also contains a UTI quadrupole mass spectrometer and an effusion gas source surrounded by a liquid H_2 cooled cryoshield, which permits dosing only the front surface of the crystal. The latter can be rotated in front of the various instruments in the vacuum system and can be cooled by means of heavy copper braids connected to the crystal supports at one end and to a coolant reservoir at the other. These braids also served as

electrical leads for heating the crystal resistively. When liquid H_2 at atmospheric pressure was used in the reservoir the crystal temperature was 26K. By pumping on the H_2 bath an ultimate temperature of 25 K could be reached.

Dosing was carried out by placing the crystal in front of the source for the appropriate time, then quickly moving it away and simultaneously pumping out the source line. Completely reproducible doses could be obtained in this way. After dosing, the crystal was rotated to face the CMA for XPS or the LEED optics for UPS. XPS data were obtained by using an SSR Instruments Model 1105 rate meter. Typical resolution in XPS was 0.2 eV using a sweep rate of 0.02 eV/sec and an electron pass energy of 50 eV. For UPS experiments the crystal was biased at -25 volts and this potential was modulated with a frequency of 10 Hz with peak to peak amplitude of 0.1 to 0.3 volts. The first and fourth LEED Grids were grounded, and the second and third grids provided the retarding field. The photoelectrons were collected at the LEED screen which was biased at +22.5 volts, and the modulated photocurrent, typically 1.5×10^{-10} amperes was amplified by a Keithley 601 electrometer. The derivative of the photocurrent with respect to the retarding field was then obtained from the output of a PAR Model HR-8 lock-in amplifier. A spectrum was taken in typically 25 minutes with an energy resolution of 0.3 eV. For all experiments reported here the He(I) line at 21.2 eV was used as the ultraviolet source; the photon-beam struck the substrate at an angle of 10° .

The crystal was cleaned by heating in oxygen and flashing in vacuum until the Auger spectrum showed no impurities. After being flashed to 2500 K with the coolant reservoir filled with liquid H_2 , the crystal cooled to its base temperature in approximately 2 minutes. In the experiments reported here, the background pressure in the vacuum chamber was less than 2.6×10^{-8} Pa (2×10^{-10} Torr)

except during UPS experiments when the helium partial pressure was 1.3×10^{-6} (1×10^{-8} Torr).

RESULTS AND DISCUSSION

Figure 1 shows a series of UPS spectra for different oxygen exposures at 26 K. For dosing times of $t \leq 80$ sec the spectrum shows a broad feature 6.6 eV below the Fermi energy, and is very similar to the spectrum of a W(110) crystal saturated with oxygen at 300K. This is shown even more clearly in the difference spectra of Fig. 2. For dosing times $t \leq 100 \leq 200$ sec peaks at 5.6, 10.1, 11.4 and 13.2 eV below ϵ_F emerge and increase in intensity. For $t \geq 200$ sec the intensity of these peaks remains unchanged, indicating saturation. At $T=25$ K it is possible to obtain indefinite increases in the intensity of these peaks, corresponding to physisorption. On heating to ~ 45 K the peaks just described disappear and a spectrum indistinguishable from a 300 K $O/W = 0.5$ layer results. A difference spectrum between a surface exposed for 80 sec (i.e., saturated with atomic oxygen) and a spectrum for 200 sec exposure (i.e., atomic plus molecular O_2) is shown in Fig. 3. There is a direct correspondence between the peaks of the difference spectrum and the gas phase He (I) ultraviolet photoelectron spectrum of O_2 . It is evident from Figure 3 that the peaks of the difference spectrum correspond to the most intense vibronic transitions in the gas phase, demonstrating that the potential curves of the electronic states are slightly, if at all, perturbed by the surface. The intensities of the peaks are also approximately the same as those in the gas phase. The difference spectrum may thus be attributed to adsorbed O_2 .

The results presented so far indicate that atomic O is adsorbed first and that adsorption of molecular O_2 occurs only after completion or near completion of this layer. This is confirmed by the XPS experiments which also permit

a more quantitative determination of the relative amounts of atomic and molecular O_2 . Fig. 4 shows a spectrum for a saturated layer deposited at 27 K. There are two main peaks, at binding energies of 536.0 and 530.5 eV respectively, relative to the substrate Fermi level. The 530.5 eV peak appears immediately upon dosing, reaches maximum intensity at $t=80$ sec and then remains constant. This peak is unchanged in position and intensity on heating to 300 K. Thus it clearly corresponds to atomic O. The 536.0 eV peak appears only for $t \geq 80$ sec and levels off for $t=200$ sec. It disappears on heating to 45 K. Thus it can be associated with molecular O_2 . The XPS results thus agree with the UPS results. The ratio of the areas under the O and O_2 peaks indicate that the number of O atoms held as molecules to those held as atoms is 1.9: 1 at ~ 27 K. On heating to 36 K for 30 seconds there is some O_2 desorption and the ratio of O atoms held as molecules to those held in the chemisorbed layer decreases to 1.1:1. These results are in reasonable agreement with the measurement of Wang and Gomer⁵ who determined the amount of O_2 desorbed at 45 K as 4.4×10^{14} O_2 molecules/cm² and that held in the chemisorbed layer as 8.8×10^{14} O atoms/cm² i.e., that the ratio is 1:1.

Leung and Gomer⁴ also found that in addition to the 45 K peak, which corresponded to a definite amount of O_2 , continued adsorption at 20 K led first to the appearance of an additional peak at ~ 27 K, which could also be saturated, and then to an indefinitely growing peak at ~ 25 K. Thus the 45 K peak corresponds, on the basis of the present interpretation to a very weakly chemisorbed O_2 species, $\alpha-O_2$, while the 27 K peak seen by Leung and Gomer, and also showing up in the present work must correspond to the first physisorbed layer. Desorption at ~ 25 K then corresponds to physisorption in a second and higher layers. As already noted some evidence for a higher layer was seen in UPS at ~ 25 K. The present experiments show that it is not possible to distinguish, either in UPS or XPS between $\alpha-O_2$ and the first two physisorbed layers. At lower tempera-

tures where thicker physisorption layers could be formed changes in level shifts would undoubtedly appear.

The UPS and XPS spectra of atomic, chemisorbed O agree with those previously seen by numerous other investigators.⁸ The spectra of α -O₂ show some interesting features, however. The UPS spectrum shows intensity distributions which conform closely to the gas phase spectrum⁹ but show slightly non-uniform level shifts toward weaker binding energy. If the work function of clean W(110) is taken as 5.30 eV, and $\Delta\phi$ for the combined atomic plus molecular layer is taken as 0.55 eV from the data of Wang and Gomer,⁵ the shifts are 0.95 eV for the ${}^2\Pi_g$ state, 0.75 eV for the ${}^4\Pi_u$ state, 0.95 eV for the ${}^4\Sigma_g^-$ state,⁹ and 1.15 eV for the ${}^2\Sigma_g^-$ state assuming that the most intense vibronic transitions in the gas phase and for adsorbed O₂ are the same. There is an uncertainty of ± 0.25 eV in the absolute, but not the relative shifts because of uncertainties in the assignment of the Fermi edge in spectra like those of Fig. 2.

The XPS spectrum also closely resembles that of gaseous O₂ including the presence of a satellite at 547 eV.¹⁰ The inset to Fig. 4 shows a high resolution spectrum of the most intense peak of α -O₂ which is split into a doublet with peaks at 535.8 eV and 537.0 eV and an approximate intensity ratio of 2:1. This also agrees with the gas phase spectrum¹⁰ where the reported splitting is 1.1 eV and the peaks are assigned to the ${}^4\Sigma^-$ and ${}^2\Sigma^-$ final states respectively.¹⁰

The absence of further splittings suggests that both O atoms in α -O₂ have the same 1 s spectrum. This in turn suggests a lying down position for α -O₂. This is also suggested by the fact that the coverage of α -O₂ is only 4.4×10^{14} O₂ molecules/cm². For a standing up position twice that coverage might well be expected.

The peaks of the XPS spectrum of α -O₂ are shifted by 1.65 eV to weaker binding energies, relative to the gas phase spectrum. This value is reasonable

for an image shift. Thus there is clearly a smaller shift for the valence levels than for the $1s$ core level. This fact, together with the slight variations in the shifts of different valence levels suggests that the principal reason for the difference lies in the greater localization of the core hole than of holes in valence orbitals.

The present results show some similarities to and some differences from the adsorption of O_2 on Pt (111) reported by Gland,² and from the adsorption on Al (111) reported by Bradshaw et al.³ On Pt a molecular entity remains up to relatively high temperature, but is clearly not physisorbed oxygen but a peroxide. There is very little shift, if any, between the $1s$ levels of chemisorbed atomic O and this molecular species. In the case of Al (111) adsorption at 30 K leads to a much broader UPS spectrum of atomic O than adsorption at 300 K, suggesting considerably more random binding at 30 than at 300 K. In addition, Bradshaw finds, as in the present work, that initial adsorption is atomic. However, for coverages in excess of 0.5 monolayers of O there is a slow conversion of molecular O_2 to atomic O. This was not seen here, although according to Wang and Gomer⁵ the total coverage of atomic O is $O/W = 0.62$ when adsorption is carried out at 20 K followed by heating to 45 K. This is slightly higher than the value of $O/W = 0.5$ obtained by adsorption at higher temperatures. Thus, there may be a small amount of conversion of $\alpha-O_2$ to atomic O on heating to 30-45K, but the amount involved is clearly less than for Al (111).

SUMMARY

The present results indicate that at 25-27 K adsorption of O_2 on W(110) leads to formation of an atomic layer. Only when this layer is saturated or nearly saturated is there evidence for the adsorption of molecular O_2 . The latter consists of a weakly bound species, $\alpha-O_2$. This is distinguishable in

thermal desorption, but not spectroscopically, from physisorbed O_2 .

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FIGURE CAPTIONS

- 1) UPS spectra of a clean and oxygen covered W(110) surface for adsorption at 26 K. Photon energy 21.2 eV. Numbers represent the dosing times.
- 2) Difference spectra, relative to that of clean W, from the data of Fig. 1. Numbers have same meaning as in Figure 1.
- 3) Difference spectrum between 200 sec dosing and 80 sec dosing curves of Figure 1. Also shown is the spectrum of gas phase O_2 , taken from Ref. 9 .
- 4) XPS spectrum of oxygen adsorption on W(110) at 27 K as function of exposure and subsequent heating, as indicated on figure. Photon source was non-monochromatized Mg $K\alpha_{1,2}$ radiation. Binding energies refer to substrate Fermi level. Structure below 525 eV is due to $K\alpha_3$, and $K\alpha_4$ satellites in the Mg radiation. Inset shows main peak of molecular O_2 at higher resolution.

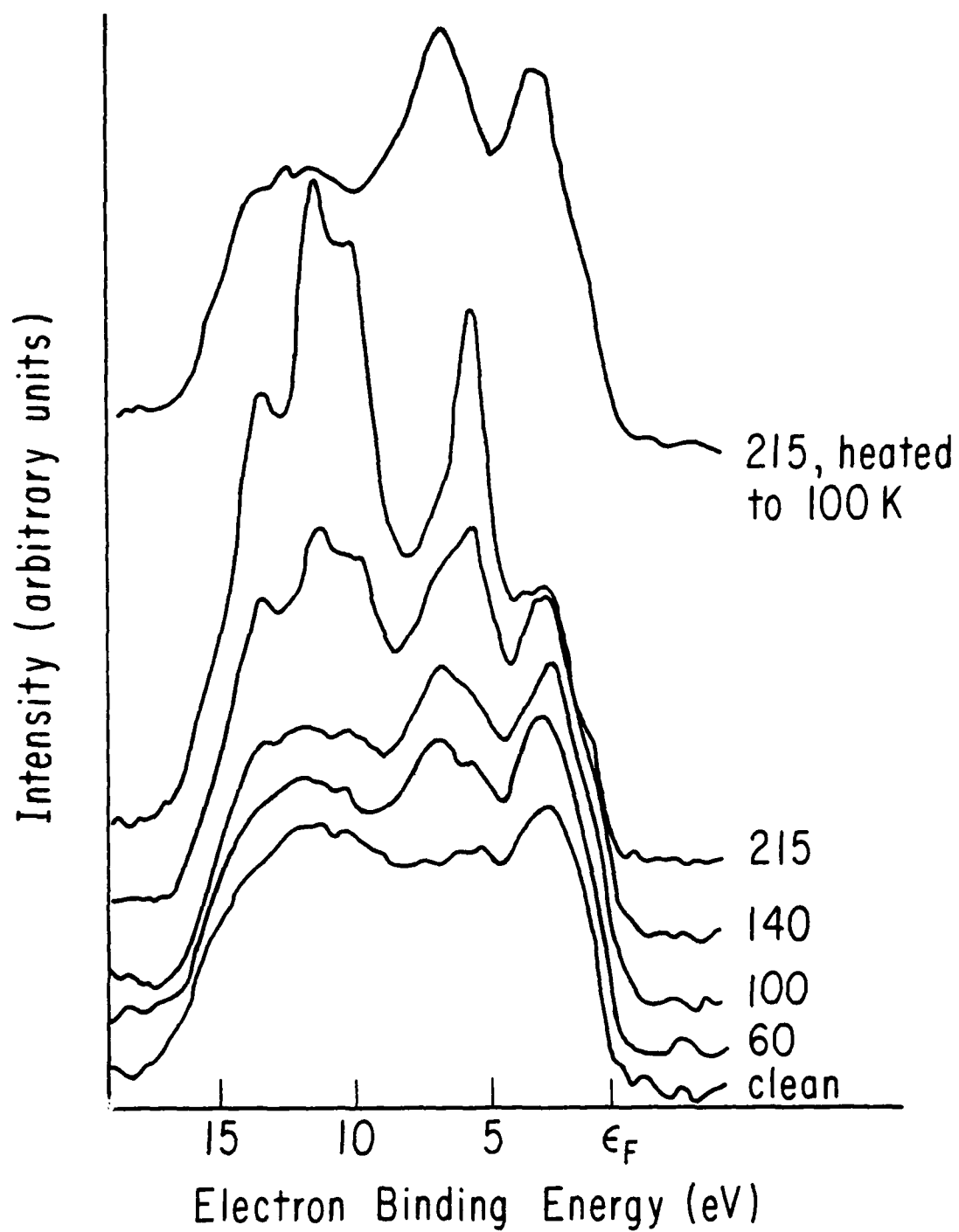


Fig.1

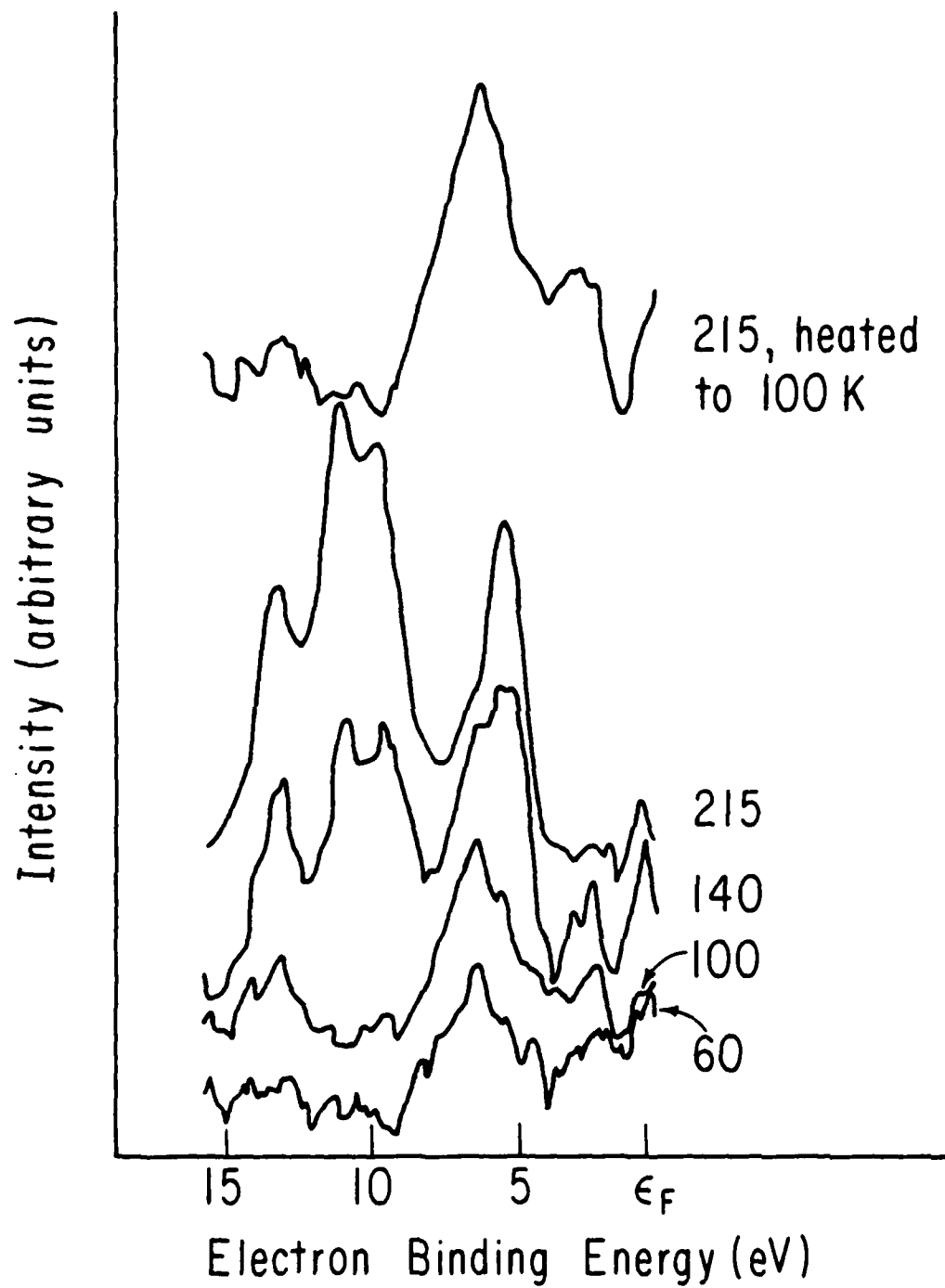


Fig.2

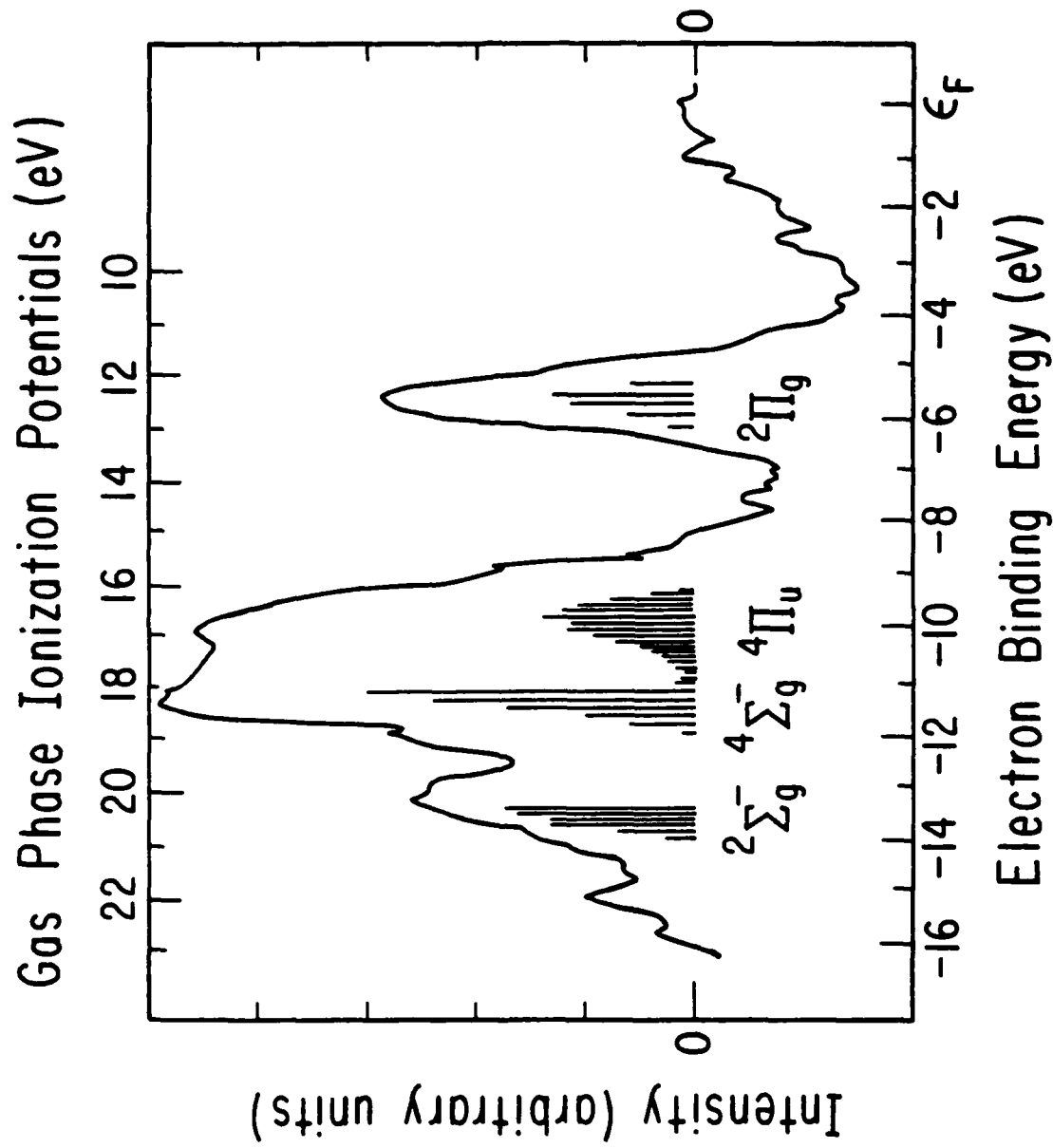


Fig.3

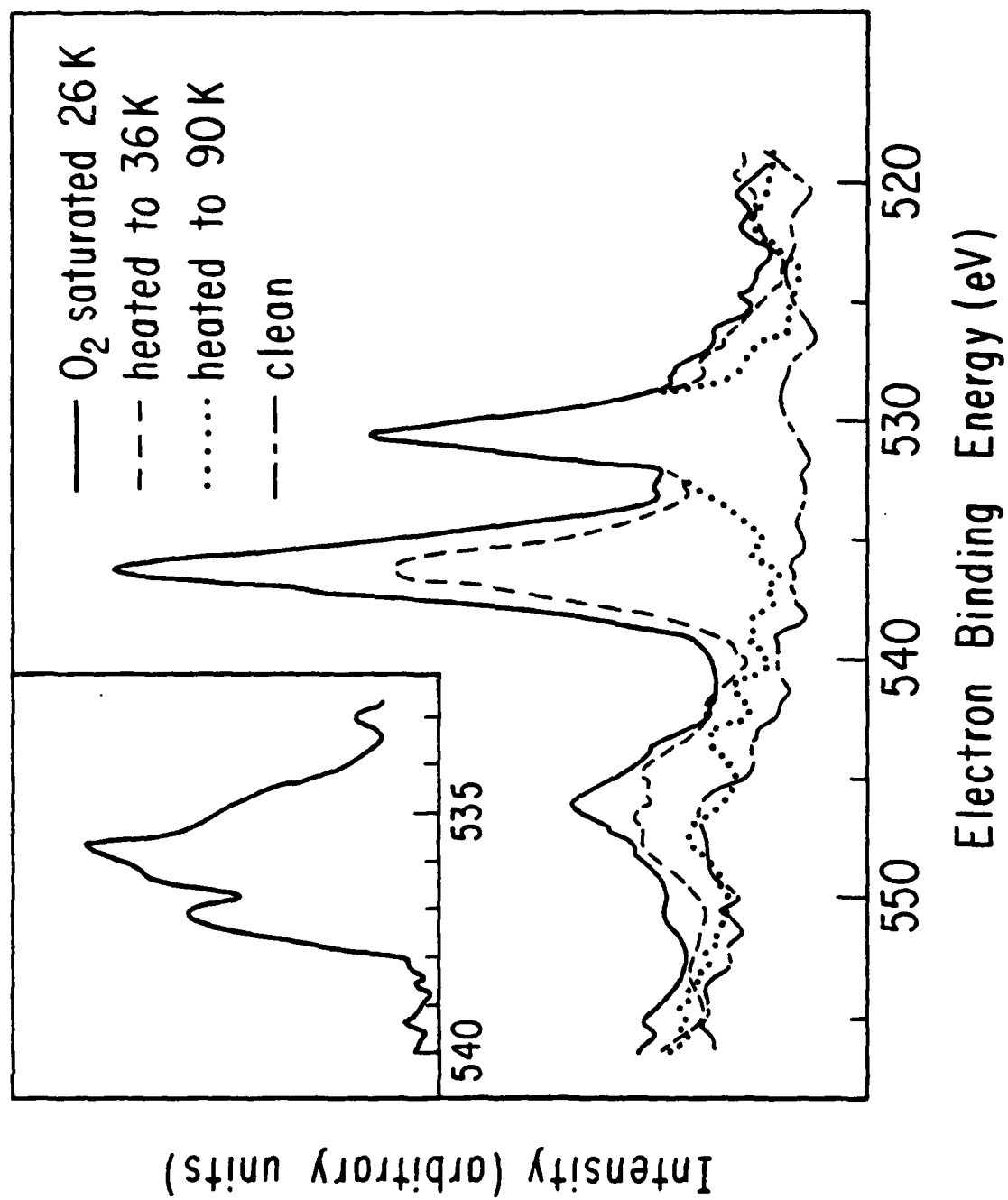


Fig. 4